

Poly[(μ_4 -5,7-dihydro-1*H*,3*H*-dithieno[3,4-*b*:3',4'-*e*]pyrazine- κ^4 N:N':S:S')tetra- μ_3 -iodido-tetra-copper]: a three-dimensional copper(I) coordination polymer

Tokouré Assoumatine^a and Helen Stoeckli-Evans^{b*}

Received 17 March 2020

Accepted 21 March 2020

Edited by A. J. Lough, University of Toronto, Canada

Keywords: crystal structure; copper(I) iodide; pyrazine; pyrazinethiophane; three-dimensional coordination polymer; framework.

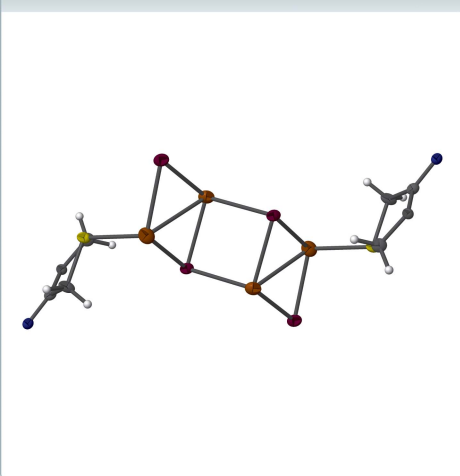
CCDC reference: 1991908

Structural data: full structural data are available from iucrdata.iucr.org

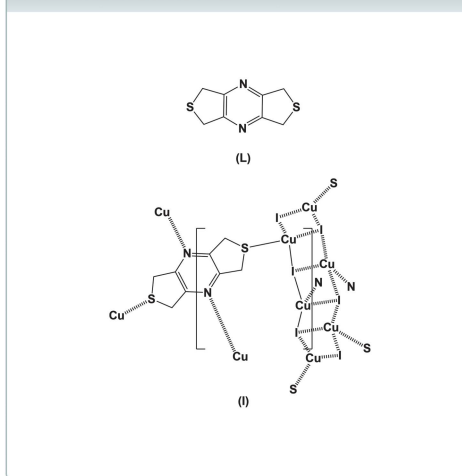
^aInstitute of Chemistry, University of Neuchâtel, Av. de Bellevaux 51, CH-2000 Neuchâtel, Switzerland, and ^bInstitute of Physics, University of Neuchâtel, rue Emile-Argand 11, CH-2000 Neuchâtel, Switzerland. *Correspondence e-mail: helen.stoeckli-evans@unine.ch

The reaction of ligand 5,7-dihydro-1*H*,3*H*-dithieno[3,4-*b*:3',4'-*e*]pyrazine (**L**) with CuI lead to the formation of a three-dimensional coordination polymer, incorporating the well known [Cu_{*x*}I_{*x*}]_{*n*} staircase motif (*x* = 4). These polymer [Cu₄I₄]_{*n*} chains are linked *via* the N and S atoms of the ligand to form the three-dimensional coordination polymer poly[(μ_4 -5,7-dihydro-1*H*,3*H*-dithieno[3,4-*b*:3',4'-*e*]pyrazine- κ^4 N:N':S:S')tetra- μ_3 -iodido-tetracopper], [Cu₄I₄(C₈H₈N₂S₂)]_{*n*} (**I**). The asymmetric unit is composed of half a ligand molecule, with the pyrazine ring located about a center of symmetry, and two independent copper(I) atoms and two independent I[−] ions forming the staircase motif *via* centers of inversion symmetry. The framework is consolidated by C—H...I hydrogen bonds.

3D view



Chemical scheme



Structure description

We have recently shown that the reaction of the ligand 5,7-dihydro-1*H*,3*H*-dithieno[3,4-*b*:3',4'-*e*]pyrazine (**L**), with silver(I) nitrate leads to the formation of a two-dimensional coordination polymer, with the silver atom coordinating only to the S atoms of the ligand so forming chains. The nitrate anion bridges two equivalent silver atoms and so generates the network structure (Assoumatine & Stoeckli-Evans, 2020*a*). Ligand **L** is one of a series of pyrazinethiophanes synthesized to study their coordination chemistry with various transition metals (Assoumatine, 1999). The reaction of **L** with CuCl₂ and CuBr₂ lead to the formation of isostructural one-dimensional coordination polymers with the ligand coordinating to the copper atom *via* the N atoms only (Assoumatine & Stoeckli-Evans, 2020*b*).

Table 1
Selected geometric parameters (Å, °).

Cu1—Cu1 ⁱ	2.7355 (16)	I2—Cu1 ⁱⁱ	2.6617 (10)
Cu1—Cu2 ⁱⁱ	2.9030 (14)	Cu2—N1 ^{iv}	2.059 (4)
Cu1—S1	2.3393 (16)	I1—Cu2 ⁱⁱ	2.6786 (9)
I1—Cu1	2.6477 (9)	I1—Cu2	2.7142 (9)
I2—Cu1 ⁱⁱⁱ	2.6478 (11)	I2—Cu2	2.6418 (8)
S1—Cu1—I1	104.34 (4)	N1 ^{iv} —Cu2—I2	107.06 (12)
S1—Cu1—I2 ^v	108.74 (5)	N1 ^{iv} —Cu2—I1 ⁱⁱ	122.19 (13)
I1—Cu1—I2 ^v	107.06 (3)	I2—Cu2—I1 ⁱⁱ	113.30 (3)
S1—Cu1—I2 ⁱⁱ	104.10 (5)	N1 ^{iv} —Cu2—I1	110.69 (13)
I1—Cu1—I2 ⁱⁱ	113.66 (3)	I2—Cu2—I1	108.98 (3)
I2 ^v —Cu1—I2 ⁱⁱ	117.98 (3)	I1 ⁱⁱ —Cu2—I1	93.48 (3)

Symmetry codes: (i) $-x + 2, -y, -z + 2$; (ii) $-x + 1, -y, -z + 2$; (iii) $x - 1, y, z$; (iv) $-x + 2, -y + 1, -z + 2$; (v) $x + 1, y, z$.

The reaction of **L** with CuI has led to the formation of a three-dimensional coordination polymer, incorporating the well known $[\text{Cu}_x\text{I}_x]_n$ staircase motif ($x = 4$; Fig. 1). The asymmetric unit is composed of half a ligand molecule, with the pyrazine ring located about a center of symmetry, and two independent copper(I) atoms and two independent I[−] ions forming the staircase motif *via* centers of inversion symmetry. The polymer $[\text{Cu}_4\text{I}_4]_n$ chains are linked *via* the N and S atoms of the ligand to form the three-dimensional framework of complex **I** (Fig. 2).

In the ligand, the five-membered thiophene rings are not planar, but have envelope configurations with the S atom as the flap. Atom S1 deviates by 0.5076 (14) Å from the mean plane of the four C atoms (C1–C4). This is considerably more than in the silver(I) nitrate two-dimensional coordination polymer or the ligand itself (Assoumatine & Stoeckli-Evans, 2020*a*). In the former, the S atom deviates from the mean plane of the four C atoms by 0.170 (15) Å, and in the latter by only 0.0256 (8) Å.

Selected bond lengths and bond angles involving the copper(I) atoms in **I** are given in Table 1. In **I**, both copper(I) atoms are fourfold coordinate; the Cu···Cu distances are not considered as bonds. Hence, atom Cu1 has a fourfold CuSI_3

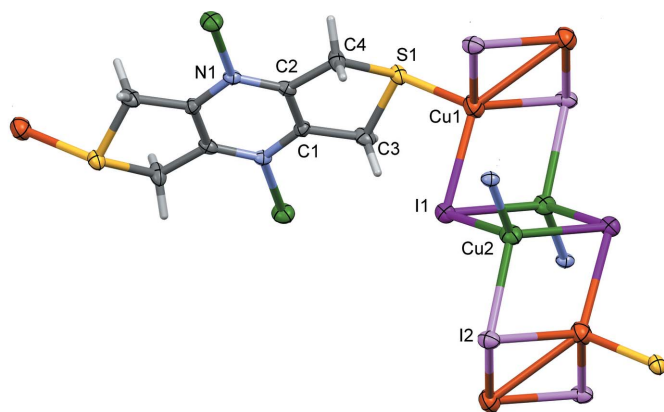


Figure 1
A partial view of the molecular structure of complex **I**, with atom labelling for the atoms of the asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level. Colour code: Cu1 orange, Cu2 green, I1 purple, I2 violet.

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3B···I1	0.97	3.01	3.808 (6)	140
C3—H3A···I1 ^{vi}	0.97	2.91	3.767 (5)	149
C4—H4A···I1 ^{iv}	0.97	3.00	3.641 (5)	124

Symmetry codes: (iv) $-x + 2, -y + 1, -z + 2$; (vi) $-x + 1, -y, -z + 1$.

coordination geometry with the fourfold index parameter $\tau_4 = 0.91$ ($\tau_4 = 1$ for a perfect tetrahedral geometry, 0 for a perfect square-planar geometry and 0.85 for perfect trigonal-pyramidal geometry; Yang *et al.*, 2007). Atom Cu2 has a CuNI_3 coordination geometry with a fourfold index parameter $\tau_4 = 0.88$. Hence, both atoms have similar distorted shapes, neither perfect tetrahedral nor perfect trigonal-pyramidal. The Cu—N, Cu—S and Cu—I bond lengths are within normal values and are discussed below.

In the crystal of **I**, the three-dimensional structure is consolidated by C—H···I hydrogen bonds (Table 2).

There are less than 15 polymeric structures in the Cambridge Structural Database (CSD; Version 5.41, last update November 2019; Groom *et al.*, 2016) that concern pyrazine ligands and the $[\text{Cu}_x\text{I}_x]_n$ staircase motif (see file S1 in the supporting information). The majority form two-dimensional coordination polymers with the pyrazine ligand bridging the $[\text{Cu}_x\text{I}_x]_n$ chains. For example, *catena*-[bis(μ_3 -iodo)(μ_2 -pyrazine-*N,N'*)dicopper(I)] (CSD refcode AGIYEU01 at 203 K; Blake *et al.*, 1999) and *catena*-[bis(μ_3 -iodo)(μ_3 -bis(6-methylpyrazin-2-ylmethyl)thioether-*N,N',N'',S*)(μ_2 -iodo)tricopper(I)] (RABBUS at 123 K; Amoore *et al.*, 2003). In AGIYEU01, the copper atom has a CuNI_3 fourfold coordination geometry with a τ_4 index parameter of 0.90. In the case of RABBUS, there are three copper(I) atoms. Two of the

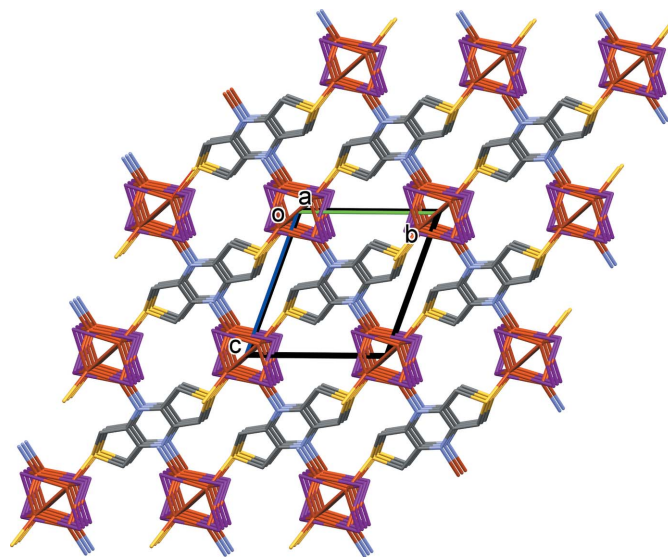


Figure 2
A view along the *a* axis of the crystal packing of complex **I**. For clarity, the H atoms have been omitted.

copper atoms have CuNI_3 fourfold coordination geometries with τ_4 index parameters of 0.92 and 0.89. The third copper atom has a CuNSI_2 fourfold coordination geometry with a τ_4 index parameter of 0.73. In comparison, the τ_4 index parameters for the two copper atoms in **I** are 0.91 and 0.85.

In AGIYEU01, the $\text{Cu-N}_{\text{pyrazine}}$ bond length is 2.028 (9) Å. In RABBUS the copper(I) atoms coordinate to the pyrazine N atoms and the S atom of the ligand. Here, the $\text{Cu-N}_{\text{pyrazine}}$ bond lengths are 2.053 (4), 2.070 (4) and 2.071 (4) Å and the Cu-S bond length is 2.3574 (15) Å. In **I**, the Cu2-N^{iv} and Cu1-S1 bond lengths of 2.059 (4) and 2.3393 (16) Å, respectively, are very similar to those sited above. The Cu-I bond lengths involving the $[\text{Cu}_x\text{I}_x]_n$ staircase motifs are very similar in all three compounds; they vary from 2.6131 (15) to 2.6485 (15) Å in AGIYEU01, from 2.5993 (7) to 2.8348 (7) Å in RABBUS, and from 2.6418 (8) to 2.7142 (9) Å in **I**. The $\text{Cu}\cdots\text{Cu}$ distances in **I**, $\text{Cu1-Cu1}^{\text{i}} = 2.7355$ (16) Å and $\text{Cu1-Cu2}^{\text{ii}} = 2.9030$ (14) Å, are similar to those in AGIYEU01 [2.7562 (19) Å] and RABUSS [2.6546 (8), 2.7565 (9) and 2.9256 (8) Å].

Synthesis and crystallization

The synthesis and crystal structure of the ligand 5,7-dihydro-1*H*,3*H*-dithieno[3,4-*b*:3',4'-*e*]pyrazine (**L**), have been reported (Assoumatine & Stoeckli-Evans, 2020*a*).

Synthesis of compound I: A solution of **L** (15 mg, 0.08 mmol) in CH_2Cl_2 (10 ml) was introduced into a 16 mm diameter glass tube and layered with MeCN (2 ml) as a buffer zone. Then a solution of CuI (15 mg, 0.08 mmol) in MeCN (5 ml) was added very gently to avoid possible mixing. The glass tube was sealed under an atmosphere of nitrogen and left in the dark at room temperature for at least 2 weeks, whereupon deep-orange plate-like crystals of the title compound, (**I**), were isolated in the buffer zone. Analysis for $\text{C}_8\text{H}_8\text{N}_2\text{S}_2\text{Cu}_4\text{I}_4$ ($M_r = 958.14 \text{ g mol}^{-1}$): calculated (%): C 10.03, H 0.84, N 2.92, S 6.69; found (%): C 10.12, H 0.80, N 2.82, S 6.67. The IR spectrum is shown in Fig. S1 of the supporting information.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. A Stoe IPDS-I one-circle diffractometer was used for the data collection at RT. With this instrument for the triclinic system often a small cusp of data is inaccessible; here 176 reflections which gives the alert *diffn_reflns_laue_measured_fraction_full_value* (0.889) below *minimum* (0.95). The effect here appears to be limited if one compares the bond lengths in the structure of the pure ligand (Assoumatine & Stoeckli-Evans, 2020*a*) with those of the ligand in complex **I**; they are the same within 3 s.u.s.

The residual electron-density peaks, $\Delta\rho_{\text{max}} = 1.73 \text{ e \AA}^{-3}$, and $\Delta\rho_{\text{min}} = -1.58 \text{ e \AA}^{-3}$, are located near the iodine atoms (within 0.80 to 1.13 Å). As stated by Spek (2018): 'they can be interpreted as absorption artefacts due to insufficient or incorrect correction for absorption'; the T_{min} and T_{max} values

Table 3

Experimental details.

Crystal data	
Chemical formula	$[\text{Cu}_4\text{I}_4(\text{C}_8\text{H}_8\text{N}_2\text{S}_2)]$
M_r	958.04
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	293
a, b, c (Å)	7.0082 (8), 8.378 (1), 8.8162 (10)
α, β, γ (°)	102.808 (13), 104.607 (13), 109.369 (13)
V (Å ³)	445.35 (10)
Z	1
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	11.87
Crystal size (mm)	0.50 × 0.35 × 0.13
Data collection	
Diffractometer	Stoe IPDS1
Absorption correction	Multi-scan (<i>MULABS</i> ; Spek, 2020)
$T_{\text{min}}, T_{\text{max}}$	0.188, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3272, 1515, 1452
R_{int}	0.038
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.612
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.040, 0.103, 1.10
No. of reflections	1515
No. of parameters	92
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	1.73, -1.58

Computer programs: *EXPOSE*, *CELL* and *INTEGRATE* in *IPDS-I* (Stoe & Cie, 1998), *SHELXS97* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2020), *SHELXL2018* (Sheldrick, 2015), *PLATON* (Spek, 2020) and *publCIF* (Westrip, 2010).

of 0.188 and 1.000, respectively, are rather extreme. However, in our experience high residual electron-density peaks are often observed for compounds containing heavy atoms such as iodine.

Acknowledgements

HSE is grateful to the University of Neuchâtel for their support over the years.

Funding information

Funding for this research was provided by: Swiss National Science Foundation and the University of Neuchâtel.

References

- Amoore, J. J. M., Hanton, L. R. & Spicer, M. D. (2003). *Dalton Trans.* pp. 1056–1058.
- Assoumatine, T. (1999). PhD Thesis. University of Neuchâtel, Switzerland.
- Assoumatine, T. & Stoeckli-Evans, H. (2020*a*). *Acta Cryst.* **E76**, 539–546.
- Assoumatine, T. & Stoeckli-Evans, H. (2020*b*). Private communications (deposition numbers 1988248 and 1988249). CCDC, Cambridge, England.
- Blake, A. J., Brooks, N. R., Champness, N. R., Cooke, P. A., Crew, M., Deveson, A. M., Hanton, L. R., Hubberstey, P., Fenske, D. & Schröder, M. (1999). *Cryst. Eng.* **2**, 181–195.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.

- Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Spek, A. L. (2018). *Inorg. Chim. Acta*, **470**, 232–237.
- Spek, A. L. (2020). *Acta Cryst.* **E76**, 1–11.
- Stoe & Cie (1998). *IPDS-1 Software*. Stoe & Cie GmbH, Darmstadt, Germany.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Yang, L., Powell, D. R. & Houser, R. P. (2007). *Dalton Trans.* pp. 955–964.

full crystallographic data

IUCrData (2020). 5, x200401 [https://doi.org/10.1107/S2414314620004010]

Poly[(μ_4 -5,7-dihydro-1*H*,3*H*-dithieno[3,4-*b*:3',4'-*e*]pyrazine- κ^4 N:N':S:S')tetra- μ_3 -iodido-tetracopper]: a three-dimensional copper(I) coordination polymer

Tokouré Assoumatine and Helen Stoeckli-Evans

Poly[(μ_4 -5,7-dihydro-1*H*,3*H*-dithieno[3,4-*b*:3',4'-*e*]pyrazine- κ^4 N:N':S:S')tetra- μ_3 -iodido-tetracopper]

Crystal data

[Cu₄I₄(C₈H₈N₂S₂)]

$M_r = 958.04$

Triclinic, *P*1

$a = 7.0082$ (8) Å

$b = 8.378$ (1) Å

$c = 8.8162$ (10) Å

$\alpha = 102.808$ (13)°

$\beta = 104.607$ (13)°

$\gamma = 109.369$ (13)°

$V = 445.35$ (10) Å³

$Z = 1$

$F(000) = 430$

$D_x = 3.572$ Mg m⁻³

Mo *K* α radiation, $\lambda = 0.71073$ Å

Cell parameters from 5000 reflections

$\theta = 3.3$ – 25.8 °

$\mu = 11.87$ mm⁻¹

$T = 293$ K

Plate, orange

$0.50 \times 0.35 \times 0.13$ mm

Data collection

Stoe IPDS-1

diffractometer

Radiation source: fine-focus sealed tube

Plane graphite monochromator

φ rotation scans

Absorption correction: multi-scan

(MULABS; Spek, 2020)

$T_{\min} = 0.188$, $T_{\max} = 1.000$

3272 measured reflections

1515 independent reflections

1452 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.038$

$\theta_{\max} = 25.8$ °, $\theta_{\min} = 3.3$ °

$h = -8 \rightarrow 8$

$k = -10 \rightarrow 10$

$l = -10 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.103$

$S = 1.10$

1515 reflections

92 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier

map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0717P)^2 + 0.7287P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 1.73$ e Å⁻³

$\Delta\rho_{\min} = -1.58$ e Å⁻³

Extinction correction: (SHELXL2018;

Sheldrick, 2015),

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.016 (3)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.57925 (5)	0.17176 (5)	0.88315 (4)	0.0210 (2)
I2	0.21064 (6)	0.27610 (5)	1.19497 (4)	0.0241 (2)
Cu1	0.90704 (13)	0.07739 (12)	0.89969 (10)	0.0309 (3)
Cu2	0.53098 (11)	0.18093 (10)	1.18047 (9)	0.0261 (2)
S1	1.0313 (2)	0.16243 (17)	0.69503 (15)	0.0198 (3)
N1	1.1948 (7)	0.6290 (6)	0.6269 (5)	0.0153 (9)
C1	0.9013 (8)	0.3374 (7)	0.5075 (6)	0.0157 (10)
C2	1.0949 (8)	0.4665 (7)	0.6316 (6)	0.0173 (10)
C3	0.8095 (8)	0.1646 (8)	0.5351 (6)	0.0227 (12)
H3A	0.759686	0.064557	0.433563	0.027*
H3B	0.689123	0.157278	0.572613	0.027*
C4	1.1768 (9)	0.4053 (7)	0.7736 (6)	0.0235 (11)
H4A	1.146935	0.457309	0.869883	0.028*
H4B	1.331493	0.439565	0.804763	0.028*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.0227 (3)	0.0192 (3)	0.0175 (3)	0.00881 (19)	0.00387 (17)	0.00296 (18)
I2	0.0207 (3)	0.0222 (3)	0.0265 (3)	0.0103 (2)	0.00545 (18)	0.00384 (18)
Cu1	0.0322 (4)	0.0328 (5)	0.0296 (4)	0.0143 (4)	0.0077 (3)	0.0158 (3)
Cu2	0.0223 (4)	0.0226 (4)	0.0229 (4)	0.0062 (3)	0.0000 (3)	0.0025 (3)
S1	0.0224 (6)	0.0158 (7)	0.0185 (6)	0.0074 (5)	0.0034 (5)	0.0057 (5)
N1	0.0137 (18)	0.018 (2)	0.0127 (19)	0.0066 (17)	0.0032 (15)	0.0036 (16)
C1	0.015 (2)	0.015 (2)	0.016 (2)	0.005 (2)	0.0047 (18)	0.0048 (19)
C2	0.017 (2)	0.020 (3)	0.014 (2)	0.010 (2)	0.0030 (19)	0.004 (2)
C3	0.020 (3)	0.026 (3)	0.016 (2)	0.009 (2)	-0.0015 (19)	0.005 (2)
C4	0.027 (3)	0.016 (3)	0.018 (2)	0.004 (2)	-0.002 (2)	0.006 (2)

Geometric parameters (\AA , $^\circ$)

Cu1—Cu1 ⁱ	2.7355 (16)	S1—C3	1.825 (5)
Cu1—Cu2 ⁱⁱ	2.9030 (14)	N1—C2	1.324 (7)
Cu1—S1	2.3393 (16)	N1—C1 ^v	1.345 (6)
I1—Cu1	2.6477 (9)	C1—C2	1.400 (7)
I2—Cu1 ⁱⁱⁱ	2.6478 (11)	C1—C3	1.478 (8)
I2—Cu1 ⁱⁱ	2.6617 (10)	C2—C4	1.509 (7)
Cu2—N1 ^{iv}	2.059 (4)	C3—H3A	0.9700
I1—Cu2 ⁱⁱ	2.6786 (9)	C3—H3B	0.9700

I1—Cu2	2.7142 (9)	C4—H4A	0.9700
I2—Cu2	2.6418 (8)	C4—H4B	0.9700
S1—C4	1.817 (6)		
Cu1—I1—Cu2 ⁱⁱ	66.05 (3)	I2—Cu2—Cu1 ⁱⁱ	57.14 (3)
Cu1—I1—Cu2	103.29 (3)	I1 ⁱⁱ —Cu2—Cu1 ⁱⁱ	56.46 (3)
Cu2 ⁱⁱ —I1—Cu2	86.52 (3)	I1—Cu2—Cu1 ⁱⁱ	105.41 (3)
Cu2—I2—Cu1 ⁱⁱⁱ	102.73 (3)	C4—S1—C3	93.7 (2)
Cu2—I2—Cu1 ⁱⁱ	66.37 (3)	C4—S1—Cu1	107.46 (19)
Cu1 ⁱⁱⁱ —I2—Cu1 ⁱⁱ	62.02 (3)	C3—S1—Cu1	109.11 (19)
S1—Cu1—I1	104.34 (4)	C2—N1—C1 ^v	115.3 (4)
S1—Cu1—I2 ^{vi}	108.74 (5)	C2—N1—Cu2 ^{iv}	121.6 (3)
I1—Cu1—I2 ^{vi}	107.06 (3)	C1 ^v —N1—Cu2 ^{iv}	123.0 (4)
S1—Cu1—I2 ⁱⁱ	104.10 (5)	N1 ^v —C1—C2	121.5 (5)
I1—Cu1—I2 ⁱⁱ	113.66 (3)	N1 ^v —C1—C3	122.6 (4)
I2 ^{vi} —Cu1—I2 ⁱⁱ	117.98 (3)	C2—C1—C3	115.9 (4)
S1—Cu1—Cu1 ⁱ	123.23 (6)	N1—C2—C1	123.2 (5)
I1—Cu1—Cu1 ⁱ	132.41 (5)	N1—C2—C4	122.9 (5)
I2 ^{vi} —Cu1—Cu1 ⁱ	59.24 (3)	C1—C2—C4	113.9 (5)
I2 ⁱⁱ —Cu1—Cu1 ⁱ	58.74 (4)	C1—C3—S1	105.0 (3)
S1—Cu1—Cu2 ⁱⁱ	121.87 (5)	C1—C3—H3A	110.7
I1—Cu1—Cu2 ⁱⁱ	57.49 (3)	S1—C3—H3A	110.7
I2 ^{vi} —Cu1—Cu2 ⁱⁱ	129.10 (4)	C1—C3—H3B	110.7
I2 ⁱⁱ —Cu1—Cu2 ⁱⁱ	56.48 (3)	S1—C3—H3B	110.7
Cu1 ⁱ —Cu1—Cu2 ⁱⁱ	94.20 (5)	H3A—C3—H3B	108.8
N1 ^{iv} —Cu2—I2	107.06 (12)	C2—C4—S1	105.1 (4)
N1 ^{iv} —Cu2—I1 ⁱⁱ	122.19 (13)	C2—C4—H4A	110.7
I2—Cu2—I1 ⁱⁱ	113.30 (3)	S1—C4—H4A	110.7
N1 ^{iv} —Cu2—I1	110.69 (13)	C2—C4—H4B	110.7
I2—Cu2—I1	108.98 (3)	S1—C4—H4B	110.7
I1 ⁱⁱ —Cu2—I1	93.48 (3)	H4A—C4—H4B	108.8
N1 ^{iv} —Cu2—Cu1 ⁱⁱ	143.81 (13)		
C1 ^v —N1—C2—C1	-0.7 (8)	N1 ^v —C1—C3—S1	164.0 (4)
Cu2 ^{iv} —N1—C2—C1	176.2 (4)	C2—C1—C3—S1	-16.8 (6)
C1 ^v —N1—C2—C4	-179.2 (5)	C4—S1—C3—C1	22.5 (4)
Cu2 ^{iv} —N1—C2—C4	-2.3 (7)	Cu1—S1—C3—C1	132.4 (3)
N1 ^v —C1—C2—N1	0.7 (8)	N1—C2—C4—S1	-164.6 (4)
C3—C1—C2—N1	-178.6 (5)	C1—C2—C4—S1	16.7 (6)
N1 ^v —C1—C2—C4	179.3 (4)	C3—S1—C4—C2	-22.5 (4)
C3—C1—C2—C4	0.1 (7)	Cu1—S1—C4—C2	-133.8 (3)

Symmetry codes: (i) $-x+2, -y, -z+2$; (ii) $-x+1, -y, -z+2$; (iii) $x-1, y, z$; (iv) $-x+2, -y+1, -z+2$; (v) $-x+2, -y+1, -z+1$; (vi) $x+1, y, z$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3B \cdots I1	0.97	3.01	3.808 (6)	140

C3—H3A···I1 ^{vii}	0.97	2.91	3.767 (5)	149
C4—H4A···I1 ^{iv}	0.97	3.00	3.641 (5)	124

Symmetry codes: (iv) $-x+2, -y+1, -z+2$; (vii) $-x+1, -y, -z+1$.